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Communication: Revised electron affinity of SF_6 from kinetic data

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Previously determined experimental data for thermal attachment of electrons to SF_6 and thermal detachment from SF_6^- over the range 590–670 K are reevaluated by a third-law analysis. Recent high precision calculations of SF_6^- harmonic frequences and anharmonicities (for several of the modes) lead to considerable changes in modeled vibrational partition functions which then have to be accommodated for by a smaller value of the derived adiabatic electron affinity EA of SF_6. The previously estimated value of EA = 1.20 (±0.05) eV in this way is reduced to a value of EA = 1.03 (±0.05) eV. In addition, the bond dissociation energy $E_{0,dis}$ for $SF_6^- \rightarrow SF_5^- + F$ is reduced to $E_{0,dis}$ = 1.44 (±0.05) eV. Finally, the consequences for modeled specific rate constants $k_{det}(E,J)$ of electron detachment from SF_6^- are discussed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3698170]

I. INTRODUCTION

The adiabatic electron affinity (EA) of SF_6 notoriously escapes an accurate determination (see Refs. 1–3 and work cited therein). On the experimental side, the high pressure mass spectrometric value of EA = 1.05 (±0.10) eV of Ref. 4 and the value of EA = 1.07 (±0.07) eV from electron capture detector studies of Ref. 5 probably were the most reliable. In our recent kinetic studies[1,6,7] of thermal electron attachment to SF_6 and thermal electron detachment from SF_6^-, we were able[1] to measure the ratio of the attachment and detachment rate constants $k_{at}/k_{det} = K_c$ over the range 590–670 K. As this range was too small to derive ΔH (and hence EA) by second-law analysis of the data, we proceeded to a third-law analysis by employing calculated rovibrational partition functions. Using vibrational frequencies and rotational constants for SF_6 and SF_6^- (both being in O_h geometry) from Refs. 8 and 9, a value of EA = 1.20 (±0.05) eV was obtained.

On the theoretical side there have been only few higher-level coupled cluster calculations, the work of Ref. 8 leading to EA = 0.92 eV while Ref. 10 led to a value of 0.90 eV. Increasing the effort, a value of EA = 0.94 eV was calculated in Ref. 2 while 0.86 eV was derived in Ref. 3. The reasons for Gaussian-G3 calculations to lead to the larger value[11] of 1.21 eV appear to be understood.[2]

In view of the unfortunate and persisting differences between experimental and theoretical estimates of EA, it appeared necessary to come back to our third-law analysis of K_c. Measurements of equilibrium constants usually offer a direct access to reaction enthalpies and the third-law analysis with estimated entropies provides a reliable procedure to analyze K_c. However, the recent quantum-chemical calculations of structural and energetic parameters of SF_6^- and SF_6 from Ref. 2 revealed quite unusual properties of SF_6^- which put the third-law analysis of Ref. 1 in question. For this reason, the present note repeats the third-law analysis of K_c from Ref. 1 on the basis of the new structural data from Ref. 2. The result is a lower value of EA than derived before, bringing experimental and quantum-chemical results into closer agreement.

II. THIRD-LAW ANALYSIS OF K_c

We base our analysis on the experimental values from Ref. 1 of $K_c/10^8$ cm^3 molecule^{-1} = 1.06, 1.96, 5.32, and 8.3 for T = 590, 620, 650, and 670 K, respectively, with the values at T = 620 and 650 K probably being most accurate. K_c = Q(e$^-$)Q(SF_6) exp(-EA/kT)/Q(SF_6^-) is calculated with the respective products Q of electronic, translational, rotational, and vibrational partition functions. The third-law analysis of Ref. 1 was made with the harmonic frequency sets of $\nu_i(SF_6)$/cm^{-1} = 779 (1), 655 (2), 965 (3), 611 (3), 519 (3), and 346 (3), and $\nu_i(SF_6^-)$/cm^{-1} = 722 (3), 626 (1), 447 (2), 306 (3), 237 (3), and 336 (3) from Ref. 8. Rotational constants A = B = C of 0.090686 cm^{-1} for SF_6 and 0.07498 cm^{-1} for SF_6^- together with symmetry numbers $\sigma(SF_6)$ = $\sigma(SF_6^-)$ = 24 were employed in addition. Fitting EA = 1.185 eV, this leads to $K_c/10^8$ cm^3 molecule^{-1} = 0.65, 1.94, 5.24, and 9.67 for T = 590, 620, 650, and 670 K, respectively, in good agreement with the experiments. This evaluation was the basis of the estimate of EA = 1.20 (±0.05) eV in Ref. 1.

While the parameters for SF_6 from the new work of Ref. 2 hardly differed from those of Ref. 8, an appreciable distortion of the equilibrium structure of SF_6^- from O_h to six equivalent minima of C_{4v} symmetry was obtained. At the same time, the frequencies of several of the modes of SF_6^- assumed considerably lower values. We, therefore, in the following first proceed to a revised third-law analysis with the harmonic frequency set of $\nu_i(SF_6)$/cm^{-1} = 787.9 (1), 654.8 (2), 966.0 (3), 617.7 (3), 526.4 (3), and 349 (3) from Ref. 2,

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being close to experimental data, and the harmonic frequency set of $\nu_i(SF_6^-)/cm^{-1} = 757.7$ (1), 597.3 (1), 506.9 (1), 224.9 (1), 479.8 (1), 263.7 (1), 371.8 (1), 671.1 (2), 435.2 (2), 240.0 (2), and 78.6 (2) from the AVTZ + d and AVQZ + d calculations of Ref. 2. The rotational constants for the C_{4v} minima of SF_6^- were[12] A = 0.07813727 cm^{-1} and B = C = 0.07391900 cm^{-1}. Because of the corresponding entropy increase of SF_6^- through lower frequency vibrations, the third-law analysis of K_c now leads to a smaller fitted value of EA. With EA = 1.077 eV, now $K_c/10^8$ cm^3 $molecule^{-1}$ = 0.79, 2.09, 5.50, and 8.72 for T = 590, 620, 650, and 670, respectively, is obtained, again well reproducing the experimental data.

The distortion of SF_6^- away from O_h geometry, besides the appearance of lower frequency modes, also results in considerable anharmonicity in several of the modes. This in turn further increases the SF_6^- entropy and lowers the fitted value of EA. Part of this effect can be treated by means of the calculation[2] of vibrational eigenstates for the 4-dimensional subsystem of the four modes of a_1 symmetry in the C_{4v} structure. These calculations, for the lowest 20 eigenstates, reached up to energies of 778.3 cm^{-1} (see Table V of Ref. 2). We empirically corrected for the truncation of the corresponding vibrational partition function, by truncating the partition function of the corresponding harmonic modes (757.7, 597.3, 506.9, 224.9 cm^{-1}) at the same energy and comparing the results with a complete partition function. We then employed the same (temperature-dependent) truncation correction factor for the anharmonic as for the harmonic system. An extension of the calculation of anharmonic energy levels of the 4-dimensional subsystem to the lowest 100 levels[12] (up to an energy of 1715 cm^{-1}) and applying the still needed truncation correction in the analogous way led to similar truncation correction factors. These were found then to give the fitted value of EA = 1.028 eV, corresponding to $K_c/10^8$ cm^3 $molecule^{-1}$ = 0.85, 2.14, 4.95, and 8.33 for T = 590, 620, 650, and 670 K, respectively, again in good agreement with the experimental K_c and their temperature dependence.

Because of the marked influences of the distortion of SF_6^- from O_h geometry and the anharmonicity of the four vibrational modes of a_1 symmetry treated so far, the given third-law analysis of K_c may not be final. Including even higher energy levels of the four modes of a_1 symmetry, i.e., refining the truncation correction factor of the partition function, and, in particular, including anharmonicities of other modes and their coupling to the a_1-modes, may lead to further changes of the derived value of EA. However, we expect these changes to be only small, in any case not being larger than ± 0.05 eV. At this stage, we therefore recommend a value of EA = 1.03 (±0.05) eV. We note that this value within the estimated error limits now agrees with the earlier experimental determinations from Refs. 4 and 5.

III. MODELING OF ELECTRON DETACHMENT FROM SF_6^-

Specific rate constants $k_{det}(E,J)$ for electron detachment from SF_6^- in Ref. 6 were calculated by combining statistical rate theory with electron attachment data. The marked influence of the value of EA on $k_{det}(E,J)$ was demonstrated.

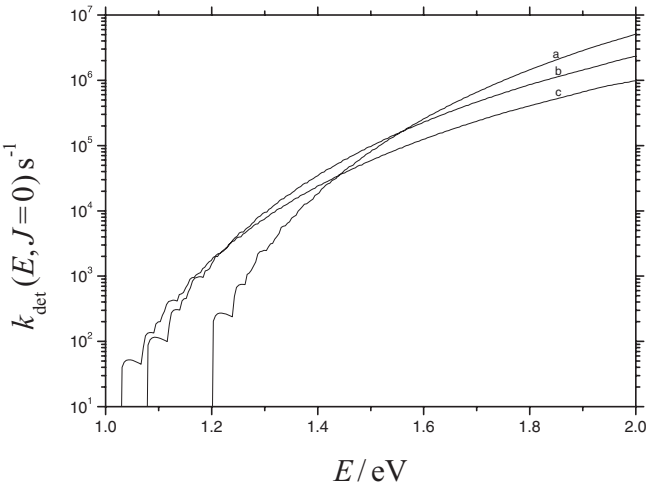

FIG. 1. Modeled specific rate constants $k_{det}(E,J = 0)$ for electron detachment from SF_6^- (curve a: results from Ref. 6 with fitted EA = 1.20 eV from Ref. 1 and harmonic oscillator frequency sets from Ref. 8 for SF_6 and SF_6^- in O_h symmetry; curve b: results from this work with fitted EA = 1.077 eV and harmonic oscillator frequency sets from Ref. 2 for SF_6 in O_h symmetry and distorted SF_6^-; curve c: results from this work with fitted EA = 1.028 eV and frequency sets with anharmonicity corrections for the four a_1-modes of distorted SF_6^- from Ref. 2, see text).

The results from statistical theory likewise also depend on the chosen set of vibrational frequencies. For this reason, it appeared worthwhile to inspect the changes in the modeled $k_{det}(E,J)$ by changes of the input parameters. Figures 1 and 2 demonstrate the results. While qualitatively the same behaviour is observed as before, quantitative differences are observed. First, there is the shift of the onset of the curves because of the changing value of EA. Second, the changing frequencies of SF_6^- influence $\rho(E,J)$ in the denominator of the statistical expression $k_{det}(E,J) = W_{det}(E,J)/h\rho(E,J)$. Partly, the two changes compensate each other. The effects of anharmonicity in curves c of the figures were treated in a simplified way by reducing the a_1-frequency 224.9 cm^{-1} by a factor of 0.25; in this way, for the four a_1-modes,

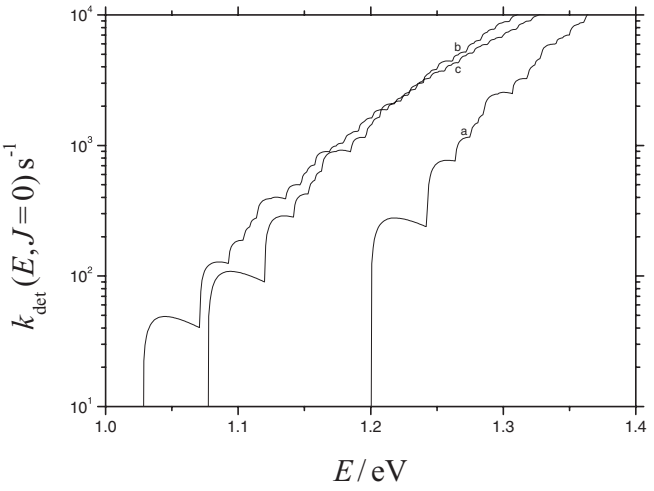

FIG. 2. Same as Fig. 1, but enlarged representation.

the same number of states $W = 10$ was obtained up to 500 cm^{-1} as with the calculated anharmonic energy levels. With increasing energy, the used effective frequency reduction factor of 0.25 increases such that curve c in the figures at high energy bends upward in the direction of curve b. Refinements of the $k_{det}(E)$ calculations will also become necessary when further anharmonicity contributions are determined. It should finally be mentioned that Figs. 1 and 2 correspond to room temperature. When other gas temperatures are considered, the modeling parameters of statistical theory (such as the parameter c_1 from Ref. 6) need to be changed. This is related to the presence of a small potential energy barrier in the nuclear coordinates which has to be accounted for, see Ref. 13. In order not to complicate the illustration this refinement was not included in Figs. 1 and 2. It has to be emphasized, however, that the presence of this barrier modifies the properties of $k_{det}(E,J)$ near to the threshold energy.

It should be noted that the dissociation energy (at 0 K) $E_{0,dis}$ of SF_6^- in the process $SF_6^- \rightarrow SF_5^- + F$ with the present change of EA also changes. In Ref. 7, a reaction enthalpy of 0.41 eV for the reaction $e^- + SF_6 \rightarrow SF_5^- + F$ was derived. With the present value for EA, this leads to $E_{0,dis} = 1.44$ (± 0.05) eV which is in good agreement with the recent high-level quantum-chemical value of 1.47 eV from Ref. 3.

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